

## COATINGS

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### ANION EXCHANGE SYNTHESIS OF SPINEL-TYPE COBALT-CONTAINING PIGMENTS

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A method is proposed for synthesizing ultramarine blue pigment by co-precipitation of cobalt and aluminum from nitrate solutions by the anion exchanger AV-17-8 in the OH form followed by roasting a precursor at 750°C for 4 h. The product obtained was studied by thermographic and x-ray radiographic analyses as well as by spectrophotometry (IR and diffuse reflection). Electron microscopy shows the pigment particles to be 50 – 80 nm in size.

**Key words:** pigment, spinel, cobalt, synthesis.

Ceramic pigments are widely used for decorating different articles made from porcelain, faience, glass and plastic and for the production of paints. Such pigments are color fast, thermally stable and chemically inert, and they resist weathering. The best ceramic pigments are obtained from spinels, which because of their crystal structure (close packing of atoms) are distinguished by resistance to high temperatures and chemical reagents [1].

The formation of spinels from hydroxides proceeds much more easily and at lower temperature because of their higher chemical activity than when oxide systems are used as precursors. The completeness of the interaction depends strongly on the degree of mixing of the initial phases, so that co-precipitation of the cations is much more preferable to mechanical mixing of hydroxides [2]. However, the hydroxide precipitates so obtained are, as a rule, contaminated with ions of the precipitant. One of the main factors determining the quality of ceramic pigments is securing the required purity of the precursors. In this connection the problem of finding new methods for synthesizing ceramic pigments is topical.

Studies have shown that one way to solve this problem is to use organic ion exchangers to effectuate synthesis. In this

case an anion exchanger serves not only as a source of the precipitation ions OH<sup>-</sup> but it also plays an important role as a factor making it possible to conduct synthesis under controllable conditions, specifically, at constant pH. In addition, in this case the product obtained does not contain impurities of the initial reagents and, therefore, does not require repeated washing and purification of the precipitate.

The present work proposes an anion-exchange method of synthesizing aluminum-cobalt spinels, consisting in precipitation of cobalt and aluminum hydroxides from solutions of the corresponding salts, when they are present simultaneously, using the strongly basic anion exchanger AV-17-8 in the OH form and subsequent roasting of the products obtained (precursors) to obtain pigments. The results obtained are compared with co-precipitation of cobalt and aluminum by a solution of NaOH.

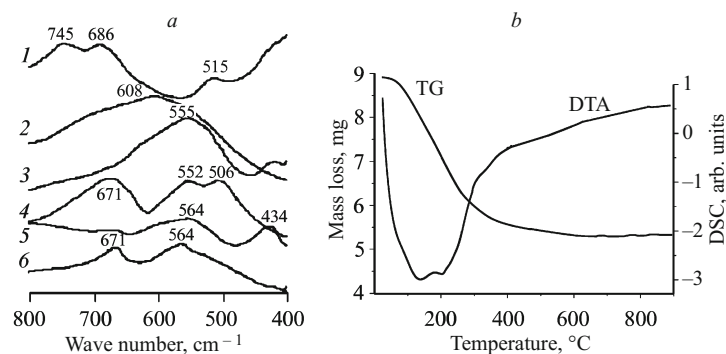
#### EXPERIMENTAL PART

The strongly basic gel anion exchanger AV-17-8 in OH form with grain size 0.25 – 0.5 mm (GOST 20301–74) and a high Donnan potential, which keeps cations from entering the sorbent phase, was used in this work. The transfer of the anion exchanger into the hydroxyl phase of the sorbent is described in [3, 4]. The total exchange capacity (TEC) of the anion exchanger was determined using 0.1 M hydrochloric acid, as described in [5].

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**Fig. 1.** IR spectra (*a*) of the samples obtained and the results of TGA studies (*b*) of sample 3: 1) cobalt hydroxide (anion exchange synthesis); 2) aluminum hydroxide (anion exchange synthesis); 3) precursor (anion exchange synthesis); 4) sample 3 after roasting at 750°C; 5) product of precipitation of cobalt and aluminum by NaOH; 6) sample 5 after roasting at 750°C.

The following method was used for anion exchange precipitation of cobalt aluminum spinel (precursor). A weighed amount of anion exchanger (TEC = 1.72 mmol-eq/g) 37.3 g was placed in contact with 50 ml (total volume) of a mixture of 0.3 M of solutions of nitrate salts of Co(II) and Al(III) (molar ratio 1 : 2) and mixed in a shaker for 3 h at room temperature. The anion exchanger was separated, passing the mixture through a sieve with opening diameter 0.25 – 0.5 mm. The precipitate was separated by filtering in a Büchner funnel in vacuum. The precipitate (precursor) obtained was dried at 110°C in a drying box.

For alkaline precipitation 50 ml of a 1 M NaOH solution was added, mixing constantly for 1 h, to 50 ml of a mixture of 0.3 M water solutions of cobalt and aluminum nitrate salts (molar ratio 1 : 2). Significant excesses of the precipitator were avoided in order to prevent any difficulties in washing the product. Vacuum filtering on a Büchner funnel was done in order to separate the precipitate. The precipitate (precursor) was dried at 110°C in drying box.

To obtain pigments the precursors were heat-treated in the interval 250 – 900°C for 4 h.

X-ray phase analysis (XPERT PRO diffractometer from the PANalytical Co., CuK $\alpha$  radiation) and IR-Fourier spectroscopy were used to identify the precipitates obtained and the products of roasting. The samples for the latter were pressed in the form of disks with spectrally pure KBr. The batches of the substance and matrix were constant; each spectrum was the result of 100 scans in the interval 450 – 4000 cm $^{-1}$  with resolution 2 cm $^{-1}$ .

Photomicrographs of the synthesized precipitates were obtained in a Hitachi S-5500 scanning electron microscope with accelerating voltage 30 kV.

Thermal analysis of the precursor was performed in air using an SDT Q600 V20.5 Build 15 thermal analyzer (resolution of the scales 0.002 g, resolution of thermocouple T: 0.1°C, DSC: 0.01  $\mu$ V).

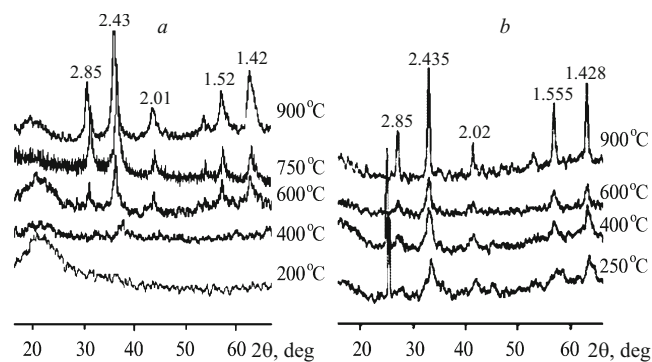
The diffuse reflection spectra in the range 200 – 800 nm were recorded with a UV-VIS-NIR Varian Cary 5000 spectrophotometer with an integrating sphere. Multistandards (Labsphere Spectralon diffuse colour standards CSS-04-020) were used for calibration.

## DISCUSSION

The precursors obtained were subjected to x-ray phase analysis. This showed that the products of synthesis were x-ray amorphous; for this reason, they were studied by IR-spectroscopy. For both the initial hydroxides and precursors a quite wide absorption band peaking in the interval 3440 – 3500 cm $^{-1}$  is observed in the IR spectra of the samples. This band is due to stretching vibrations of the hydroxyl groups. The most informative IR region (from 400 to 800 cm $^{-1}$ ) is presented in Fig. 1*a*. For a precursor obtained using an anion exchanger an absorption band is observed at 555 cm $^{-1}$ , which is characteristic for octahedrally coordinated aluminum [AlO $_6$ ]. Usually, it is encountered in the spectra of spinels CoAl $_2$ O $_4$  [7], but it is also present in the IR spectrum of the pigment obtained by roasting the precursor at 750°C (Fig. 1*a*, curve 4). In addition, this band is absent in the initial cobalt and aluminum hydroxides (Fig. 1*a*, curves 1 and 2) and in precursor obtained by alkaline precipitation (Fig. 1*a*, curve 5). Therefore, the interaction of the hydroxides and the formation of the spinel structure already start at the anion exchange synthesis stage [2]. In addition, after roasting new absorption bands appear at 506 and 671 cm $^{-1}$  in the precursor spectrum (Fig. 1*a*, curve 4); these bands are also characteristic for the spinel CoAl $_2$ O $_4$  [7].

A peak at 434 cm $^{-1}$  due to stretching vibrations of the bond Al–O in Al $_2$ O $_3$  is observed in the precipitate of the precursor obtained by alkaline precipitation (Fig. 1*a*, curve 5). The shoulder in the interval 540 – 580 cm $^{-1}$  corresponds to the vibration of the octahedrally coordinated cobalt in Co $_3$ O $_4$  [15]. After roasting at 750°C the corundum bands in the spectrum vanish, and one other peak associated with the vibration of the tetrahedrally coordinated cobalt in Co $_3$ O $_4$  appears at 671.7 cm $^{-1}$ . Thus, in the present case, together with the aluminum-cobalt spinel a significant amount of cobalt oxide (II, II) is present in the product and masks the pigment color (the precipitate is black after roasting).

Thermographic analysis of the precursor obtained by anion-exchange synthesis (Fig. 1*b*) shows that the mass change of the precipitate (from 8.916 to 5.383 mg) is associated with the degradation of the initial hydroxides (endo effect at  $T$  = 130 and 210°C on the DTA curve); no effects are observed on subsequent heating to 900°C, which is due to the



**Fig. 2.** X-ray spectra of the precursors obtained using an anion exchanger (a) and alkaline precipitation (b) with different roasting temperatures.

thermal stability of the pigment. Also absent are extrema corresponding to crystallization of the spinel structure. In this connection the onset temperature of crystallization of  $\text{CoAl}_2\text{O}_4$  was determined experimentally, roasting the precursor in the temperature interval 250 – 900°C and performing an x-ray diffraction analysis of the product.

It is evident in Fig. 2a that the diffraction peak (2.43) characteristic for spinel  $\text{CoAl}_2\text{O}_4$  already appears at the roasting temperature 400°C. After roasting at 600°C the number of spinel lines increases (the diffraction peaks at (2.85), (2.01), (1.5) and (1.425) [9]), and their intensity increases with subsequent increases of the roasting temperature (750 and 900°C). For roasting at 750°C the product color changes to ultramarine blue, characteristic for these compounds, and remains unchanged with subsequent increases of the roasting temperature. Thus, in the case of anion exchange precipitation of the precursor the spinel structure forms at a lower temperature (750°C) than described in the literature. Thus, in [7] it is reported that  $\text{CoAl}_2\text{O}_3$  was obtained by self-propagating high-temperature synthesis at 1400°C while in [6], where the sol-gel method was used, the spinel lines were recorded at 1000°C; the products of solid-phase synthesis gave spinel only after roasting at 1300°C [12].

The x-ray diffraction patterns of a sample obtained by alkaline precipitation (Fig. 2b) show a peak which is characteristic for  $\text{NaNO}_3$  impurity [10]; after roasting at 600°C this peak vanishes because this impurity undergoes thermal de-

composition. The other peaks are impossible to assign unequivocally to any compound, since the diffraction peaks of cobalt aluminum spinel and  $\text{Co}_3\text{O}_4$  coincide [11]. On the basis of the results obtained we suppose that the black product formed as a result of alkaline precipitation is a mixture of spinel and  $\text{Co}_3\text{O}_4$ .

According to the results of scanning electron microscopy (Fig. 3a) the pigment particles are agglomerated into larger, nearly spherical formations 30 – 80 nm in size. Thus, the anion exchange method of synthesis gives a highly disperse product that does not require additional comminution.

Color is one of the most important properties of a pigment [13, 14]. The color coordinates were determined from the diffuse reflection spectrum (Fig. 3b):  $L^* = 25.44$ ,  $a^* = 12.34$  and  $b^* = 35.89$ . The color coordinates  $a^*$  and  $b^*$ , corresponding to the green and blue branches, respectively, are slightly greater (for  $a^*$ ) or less (for  $b^*$ ) than for the blue standard ( $a^* = 8.04$  and  $b^* = 16.86$ , CSS-04-020), i.e., the color of the pigment obtained (ultramarine blue) is shifted somewhat into the green region compared with the blue standard.

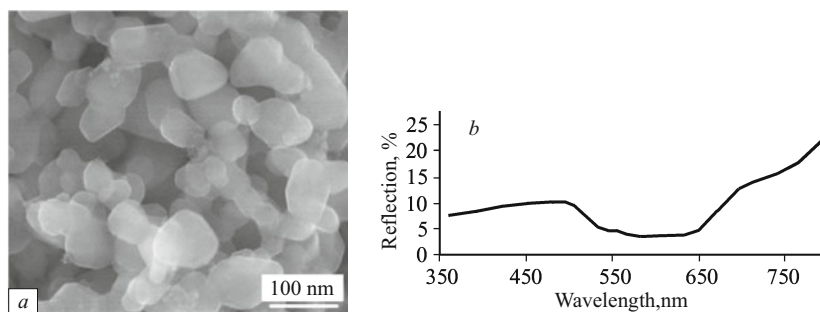
It should be noted that co-precipitation of cobalt and aluminum by alkali does not lead to the formation of pigment. Instead, a mixture of the spinel and the black oxide  $\text{Co}_3\text{O}_4$ , contaminated with sodium salt, is formed.

In summary, a method was developed for synthesizing ultramarine blue pigment from cobalt and aluminum nitrate salts with both present simultaneously, using the anion exchanger AV-17-8 in OH form followed by roasting of the product at temperature 750°C. This pigment is thermally stable and can be used in the production of over- and under-glaze paints.

*This work was performed using apparatus from the Krasnoyarsk Regional Apparatus Sharing Center of the Siberian Branch of the Russian Academy of Sciences.*

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**Fig. 3.** Photomicrograph of the pigment  $\text{CoAl}_2\text{O}_4$  obtained at roasting temperature 750°C (a) and its diffuse reflection spectrum (b).

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